

EXPRESS MAIL LABEL NUMBER EL822429080US

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Form PTO-1390 REV.10-94)		U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE	ATTORNEYS DOCKET NUMBER RN98173
TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/elected office (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371			U.S. APPLICATION NO. (F. KNOWN, SEE 3737 CFR 1.9) 09/857578 NOT APPLICABLE
INTERNATIONAL APPLICATION NO. PCT/FR99/02984	INTERNATIONAL FILING DATE December 1, 1999	PRIORITY DATE CLAIMED December 9, 1998	
TITLE OF INVENTION PEROXIDE-COMPRISING POLYORGANOSILOXANES (POS), ONE OF THEIR PROCESSES OF PREPARATION AND THEIR USES, IN PARTICULAR AS BLEACHING AGENT IN DENTAL COMPOSITIONS			
APPLICANT (S) FOR DO/EO/US: Adrien DROMARD, Gérard MIGNANI, Lucile GAMBUT, and Frédéric DALLEMER			
Applicant herewith submits the United States Designated/Elected Office (DO/EO/US) the following items and other information:			
1 <input checked="" type="checkbox"/> This is a FIRST submission of items concerning a filing under 35 U S C 371 2 <input type="checkbox"/> This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U S C 371 3 <input checked="" type="checkbox"/> This express request to begin national examination procedures (35 U S C 371) (f) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U S C 371 (b) and PCT Articles 22 and 39(1) 4 <input checked="" type="checkbox"/> A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date 5 <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U S C 371(c)(2)) a. <input type="checkbox"/> is transmitted herewith (required only if not transmitted by the International Bureau). b. <input checked="" type="checkbox"/> has been transmitted by the International Bureau. c. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US) 6 <input checked="" type="checkbox"/> A translation of the International Application into English (35 U S C 371(c)(2)). 7 <input checked="" type="checkbox"/> A copy of the International Search Report (PCT/ISA/210) 8 <input checked="" type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U S C 371(c)(2)). a. <input type="checkbox"/> are transmitted herewith (required only if not transmitted by the International b. <input type="checkbox"/> have been transmitted by the International Bureau c. <input type="checkbox"/> have not been made, however the time limit for making such amendments has NOT expired. d. <input checked="" type="checkbox"/> have not been made and will not be made. 9 <input type="checkbox"/> A translation of the amendments to the claims under PCT Article 19 (35 U S C 371(c)(3)). 10 <input checked="" type="checkbox"/> A oath or declaration of the inventor(s) (35 U S C 371(c)(4)). (unsigned) 11 <input checked="" type="checkbox"/> A copy of the International Preliminary Examination Report (PCT/IPEA/409). 12 <input type="checkbox"/> A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U S C 371(c)(5)). Items 13 to 18 below concern document(s) or information included: 13 <input checked="" type="checkbox"/> An information Disclosure Statement under 37 CFR 1.97 and 1.98 14 <input type="checkbox"/> An assignment document for recording A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included 15 <input checked="" type="checkbox"/> A FIRST preliminary amendment 16 <input type="checkbox"/> A SECOND or SUBSEQUENT preliminary amendment 17 <input type="checkbox"/> A substitute specification. 18 <input type="checkbox"/> A change of power of attorney and/or address letter 19 <input checked="" type="checkbox"/> Certificate of Mailing by Express Mail 20 <input checked="" type="checkbox"/> Other items or information Forms PCT/IB/308 and 332, PCT/ISA/ 210 (English & French Version), PCT/IPEA/ 409, PCT/FR99/02984 as published			

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Serial No. National Phase of PCT/FR99/02984 Intern. Filing date December 01, 1999	Filing Date June 07, 2001	Examiner N/A	Group Art Unit N/A
Invention: PEROXIDE-COMPRISING POLYORGANOSILOXANES (POS), ONE OF THEIR PROCESSES OF PREPARATION AND THEIR USES, IN PARTICULAR AS BLEACHING AGENT IN DENTAL COMPOSITIONS			
I hereby certify that this Transmittal letter sending documents referred to herein, Specification with Abstract (62 pages), Declaration/ Power of Attorney (unsigned), Preliminary Amendment (9 pages), Information Disclosure Statement with copy of 4 references, Forms PCT/IB/ 306, 308 and 332, PCT/IPEA/409 & 416, Forms PCT/ISA/210 (English & French Version), PCT/FR99/02984 as published.			
<p align="center"><i>(Identify type of correspondence)</i></p> <p>is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10 in an envelope addressed to: The Assistant Commissioner for Patents, Washington, D.C. 20231 on <u>June 07, 2001</u>.</p> <p align="right">(Date)</p> <p align="right">  Vincent BOITTIAUX <i>(Typed or Printed Name of Person Mailing Correspondence)</i> </p> <p align="right">_____ <i>(Signature of Person Mailing Correspondence)</i> </p> <p align="right"> EL822429080US <i>("Express Mail" Mailing Label Number)</i> </p> <p align="center">Note: Each Paper must have its own certificate of mailing.</p>			

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Case RN98173

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In the Application of: Adrien DROMARD, Gérard MIGNANI, Lucile
GAMBUT, and Frédéric DALLEMER

National Phase of PCT/FR99/02984

International Filing Date : December 01, 1999

Serial No: N/A

Filing Date: June 07, 2001

For: PEROXIDE-COMPRISING POLYORGANOSILOXANES (POS), ONE
OF THEIR PROCESSES OF PREPARATION AND THEIR USES, IN
PARTICULAR AS BLEACHING AGENT IN DENTAL COMPOSITIONS

Assistant Commissioner for Patents
Washington, D.C. 20231

PRELIMINARY AMENDMENT

Dear Sir:

Prior to calculation of filing fee, please enter the following amendment in the
specification and claims:

In the specification:

Page 1, just after the title, please add the following paragraph:

This application is an application under 35 U.S.C. Section 371 of International
Application Number PCT/FR99/02984 filed on December 01, 1999.

In the claims:

Please cancel claims 1 to 14 and replace them with the following new claims 15 to 39 :

15. (New) Polyorganosiloxanes (POSSs) comprising siloxane units having the
following formula (I):

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- $a + b + c$ is from 0 to 3,
- a , b and c are from 0 to 3,
- R , which is identical or different, is a monovalent hydrocarbonaceous group,
- E , which is identical or different, is a monovalent functional substituent, carrying one or more peroxo(-O-O-) functional group F_{po} ,
- G , which is identical or different, is a functional substituent comprising one or more F_{po} -stabilizing functional group F_{stab} , which are identical to or different from one another, capable of bonding via weak bonds with the F_{po} functional group,
- the concentration $\{F_{po}\}$ of F_{po} functional groups, expressed by the ratio

$$\{F_{po}\} = \frac{F_{po} \text{ number}}{\text{Total number of silicon atoms in the POS}},$$
 is greater than 0, and
- the concentration $\{T \text{ and/or } Q\}$, as mol%, of units selected from the group consisting of T units and Q units, is from 0 to 20, T units being defined as siloxane units wherein $a+b+c=1$, and Q units being defined as siloxane units wherein $a+b+c=0$.

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16. (New) Polyorganosiloxanes according to claim 15, wherein R is a linear C₁-C₄ alkyl group, a branched C₁-C₄ alkyl group, a phenyl group, a xylyl group or a tolyl group.
17. (New) Polyorganosiloxanes according to claim 15, whereat least one E substituent further comprises one or more Fpo-stabilizing functional group Fstab, which are identical to or different from one another, and capable of bonding via weak bonds with the Fpo functional group.
18. (New) Polyorganosiloxanes according to claim 15, wherein $0.1 \leq \{Fpo\} \leq 0.6$.
19. (New) Polyorganosiloxanes according to claim 15, wherein $0 \leq \{T \text{ and/or } Q\} \leq 8$.
20. (New) Polyorganosiloxanes according to claim 15, wherein:
- E, which is identical or different, is selected from the group consisting of (cyclo)aliphatic hydrocarbonaceous groups, aromatic hydrocarbonaceous groups and heterocyclic hydrocarbonaceous groups, said groups comprising, optionally, one or more heteroatom and being, optionally, substituted, and
 - the Fpo group is included:

- in an acyl peroxide of the following formula,
$$\begin{array}{c} \text{---C---OOX} \\ || \\ \text{O} \end{array}$$
, wherein X is hydrogen, or an aliphatic, alicyclic, aromatic, or heterocyclic monovalent hydrocarbonaceous radical comprising hydrogen and carbon atoms, and, optionally, one or more heteroatom, said radical being optionally substituted, or

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- in a peroxide residue comprising an oxygen carrier selected from the group consisting of sulfur, phosphorus, silicon and boron.

21. (New) Polyorganosiloxanes according to claim 20, wherein the heteroatom is N, S, or O.

22. (New) Polyorganosiloxanes according to claim 20, wherein X is a radical having the same definition than R in formula (I), a halogen atom, or a cation forming a salt with peroxo anions.

23. (New) Polyorganosiloxanes according to claim 22, wherein X is an elements from columns Ia and IIA of the Periodic Table.

24. (New) Polyorganosiloxanes according to claim 15, wherein Fstab generates weak bonds (hydrogen bonds) with Fpo functional groups, and is selected from the group consisting of:

- functional units comprising nitrogen, oxygen, fluorine, sulfur or phosphorus,
- cationic units,
- chelating units comprising one or more ether or amine functional group,
- phosphonate chelating units, and
- sulfonate chelating units.

25. (New) Polyorganosiloxanes according to claim 15, wherein Fstab generates weak bonds (hydrogen bonds) with Fpo functional groups, and is selected from the group consisting of carboxylic units, carboxylate units, amide units, imide units, sulfonamide

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units, hydroxyl units, alkoxy units, amine units, organofluorinated units, and quaternary ammoniums units.

26. (New) Polyorganosiloxanes according to claim 15, of the following formula (II):



wherein

- R^1 and R^3 , which are identical or different, are hydrogen, a hydroxyl or a monovalent a hydrocarbonaceous group,
- R^2 , which is identical or different, is hydrogen, hydroxyl, or a monovalent a hydrocarbonaceous group,
- $2 \leq m + n + o \leq 300$,
- $0 \leq m \leq 200$,
- $0 \leq n \leq 50$, and
- $0 \leq o \leq 50$.

27. (New) Polyorganosiloxanes according to claim 26, wherein

- $3 \leq m + n + o \leq 50$,
- $1 \leq m \leq 100$,
- $1 \leq n \leq 10$, and
- $1 \leq o \leq 10$.

28. (New) Polyorganosiloxanes according to claim 26, wherein

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- $5 \leq m + n + o \leq 20$,
- $1 \leq m \leq 10$,
- $2 \leq n \leq 4$, and
- $2 \leq o \leq 4$.

29. (New) Polyorganosiloxanes according to claim 26, wherein:

- R^1 and R^3 are a C_1 - C_3 alkyl,
- R^2 is a C_1 - C_3 alkyl, and
- E carries Fpo and Fstab functional groups.

30. (New) Polyorganosiloxanes according to claim 29, wherein R^1 , R^2 and R^3 are methyl groups.

31. (New) Polyorganosiloxanes according to claim 15, wherein E further carries at least one bicarboxylated, benzoxyl or imide unit.

32. (New) A process for the preparation of the polyorganosiloxanes according to claim 15, essentially consisting in oxidizing polysiloxane precursors of the polyorganosiloxanes according to claim 15, comprising a step of oxidizing with an agent selected from the group consisting of H_2O_2 , O_2 , O_3 and their mixtures, the polysiloxane precursors being distinguished from the polyorganosiloxanes comprising peroxo groups according to claim 15 in that they comprise one or more F'po functional groups which are Fpo functional group precursors and are composed of:

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- carboxyl residues of formula $\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{O}-\text{X}' \end{array}$ wherein X' is hydrogen, or an aliphatic, alicyclic, aromatic, or heterocyclic monovalent hydrocarbonaceous radical comprising hydrogen and carbon atoms, and, optionally, one or more heteroatom, said radical being, optionally, substituted,

- acid anhydride residues of formula $\begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ -\text{C}-\text{O}-\text{C}- \end{array} ;$,
- aldehyde residues, or
- oxide residues comprising sulfur, phosphorus, silicon or boron.

33. (New) A process according to claim 32, wherein the polysiloxanes precursors carry functional substituents selected from the group consisting of:

- anhydride substituents
- carboxyl substituents,
- aldehyde substituents,
- sulfonyl substituents,
- phosphoryl substituents,
- siloxyl substituents, and
- boroxide substituents.

34. (New) A process according to claim 33, wherein the polysiloxanes precursors carry

- anhydride groups, the oxidation being carried out with H_2O_2 in the presence of a strong base catalyst, or

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- carboxylic groups, the oxidation being carried out with H_2O_2 in the presence of a strong acid catalyst.

35. (New) A process according to 32, wherein polysiloxanes precursors are used with a molar purity greater than or equal to 90%.

36. (New) A process according to 32, wherein polysiloxanes precursors are used with a molar purity greater than or equal to 95%.

37. (New) Polysiloxanes precursors as defined in claim 32.

38. (New) A dental composition, comprising polyorganosiloxanes according to claim 15.

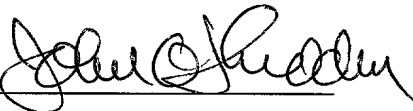
39. (New) A detergent composition, comprising polyorganosiloxanes according to claim 15.

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REMARKS

These preliminary amendments are filed to comply with the claims structure and wording according to the United States Law. It is asserted that these amendments do not add new matter. Support for these amendments can be found in the specification and claims as originally filed. Entry of these amendments is respectfully requested.

Respectfully submitted,

By 

June 5, 2001

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**PEROXIDE-COMPRISING POLYORGANOSILOXANES (POS), ONE OF
THEIR PROCESSES OF PREPARATION AND THEIR USES, IN
PARTICULAR AS BLEACHING AGENT IN DENTAL COMPOSITIONS**

5 The field of the invention is that of
peroxide-comprising systems which can be applied in
particular in bleaching, disinfecting, cleaning or the
initiation of polymerizations (for example radical
polymerization) or of epoxidation reactions. The
10 oxidizing properties of these systems are more
particularly valued in bleaching applications, in
particular dental (e.g. dentifrice) or detergent
applications.

 The peroxide-comprising systems targeted in
15 the context of the present account are functionalized
polymers.

 The present invention relates to peroxide-
comprising polyorganosiloxanes (POS) and to one of
their processes of preparation.

20 The invention also relates to silicone
precursors of these peroxide-comprising POSs.

 Finally, the present invention comprises an
application aspect which comprises the use of peroxide-
comprising POSs according to the invention as active
25 ingredient in bleaching, disinfecting, cleaning and the
initiation of chemical reactions. More specifically,
the invention is targeted at dental compositions, for

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example dentifrices, or detergent compositions comprising peroxide-comprising POSs as bleaching agent.

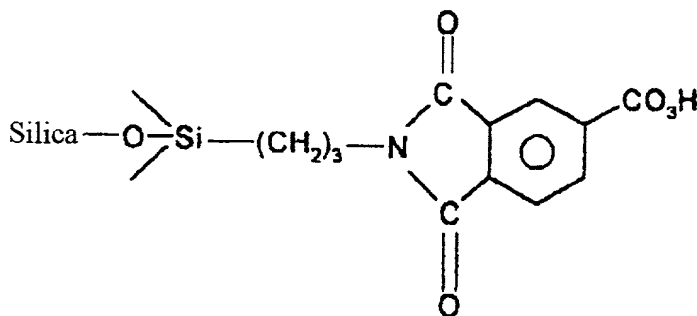
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The use is known of hydrogen peroxide H_2O_2 or its persalts (calcium peroxides, perborates, 5 percarbonates) in the field of bleaching, in particular dental bleaching. In the continuation of the present account H_2O_2 will denote H_2O_2 as such or its persalts. The disadvantages of hydrogen peroxide are not insignificant. Firstly, H_2O_2 has to be employed at a 10 high concentration to be effective. This point is particularly annoying because of the aggressiveness of H_2O_2 . Secondly, it is known that the bleaching action is related to the oxygen-donating effect. In point of fact, this effect is not the predominant effect which 15 can be obtained with hydrogen peroxide. The latter behaves essentially as a promoter of deleterious free radicals which do not participate in the bleaching function and which instead would even have a tendency to interfere with it. Thirdly, hydrogen peroxide has 20 the disadvantage of being unstable.

There thus exists a clearly identified need for a substitute of hydrogen peroxide for these applications in the field of bleaching and in particular of dental bleaching (dentifrices).

25 In attempting to solve the problem targeted above, patent US No. 5 698 326 has provided peracid

5 trimellitic anhydride, the carboxylic functional group of the benzyl nucleus of which is subsequently oxidized to convert it to a peracid functional group. This corresponds to the following formula:



According to this patent, the grafting of the peracid functional group to the inorganic support made of silica is sensible to make possible stabilization of the peracid functional group. In reality, it turns out that this stability might be further improved. In addition, there is reason to fear that these peroxide-comprising silicas are difficult to disperse in relatively viscous compositions, such as dentifrices. European patent application No. 796 874 relates to a process for the preparation of polymers comprising peroxy-carboxylic groups. These peroxy-carboxylic polymers are more specifically

N-vinylpyrrolidone/maleic anhydride copolymers.

Hydrogen peroxide, which is reacted with this copolymer, makes it possible to convert carboxyls resulting from anhydride to peroxy-carboxylic functional

5 groups. The performance of these peroxy-carboxylated copolymers in terms of bleaching was not revealed by this patent application. Furthermore, it seems that, in the dental bleaching application, peroxy-carboxylated copolymers lack selectivity with regard to teeth. In
10 addition, problems of instability may be feared for dental bleaching applications of these copolymers.

Patent application PCT WO 97/02 011 discloses dental oral compositions comprising conventional ingredients, such as abrasives, binders, humectants,
15 surfactants, sources of fluorine ions or other sweeteners and two other essential ingredients, namely, first, an aminoalkylsilicone, such as a polydimethylsiloxane comprising aminoalkyl units of the propylaminoethylamine type in the chains and at their
20 ends, and, secondly, a polydimethylsiloxane comprising pendant groups of polyoxyethylene and/or polyoxypropylene type having a surfactant action.

No mention is made in this document of polyorganosiloxanes functionalized by peroxide units.
25 This oral composition is presented as having improved antiplaque and antibacterial properties, which

complement an excellent cleaning performance. This oral composition can also comprise bleaching agents belonging to the family of inorganic peracid salts (metal persulfates, perborates, percarbonates and 5 peroxides).

These oral compositions are not satisfactory as regards stability, toxicity, selectivity with respect to teeth and effectiveness of bleaching by oxidation.

In such a state of the art, one of the 10 essential objects of the inventors was to develop a novel oxidizing system which can be used in particular in bleaching, for example dental or detergent bleaching, in disinfection, in cleaning or in the initiation of chemical reactions, this oxidizing system 15 of peroxide-comprising type having to be more stable and more effective than the known systems of the prior art.

Another essential object of the invention is to provide a peroxide-comprising bleaching system, in 20 particular for dental bleaching applications, which makes it possible to control the reactivity of the peroxide functional group, so as to limit as much as possible its conversion to aggressive free radicals.

Another essential object of the invention is 25 to provide a peroxide-comprising bleaching system which

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can be used in particular in dental bleaching and which has a significantly improved stability on storage.

Another essential object of the invention is to provide a peroxide-comprising bleaching system,
5 applied in dental bleaching (oral composition for the treatment and maintenance of the teeth), having a better selectivity with respect to teeth to be bleached.

Another essential object of the invention is
10 to provide a peroxide-comprising oxidizing system capable of being used as a system for the controlled release of oxidizing peroxide functional groups, indeed even of free radicals which initiate chemical reactions.

15 Another essential object of the invention is to provide a process for the production of the abovementioned peroxide-comprising oxidizing system which is simple to employ and economic.

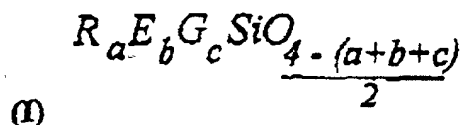
Another essential object of the invention is
20 to stipulate the use of the peroxide-comprising oxidizing system targeted above as bleaching agent, as disinfecting agent, as cleaning agent or as agent for the initiation of chemical reactions.

Another essential object of the invention is
25 to provide a dental composition possessing an effective, stable and selective bleaching agent.

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Another essential object of the invention is to provide a detergent composition comprising an effective, stable and economic bleaching agent.

These objects, among others, are achieved by the present invention, which relates to novel polyorganosiloxanes (POSs) comprising siloxane units of following formula (I):



→ in which

- $a + b + c = 0$ to 3
- $a, b, c = 0$ to 3
- R corresponds to one or more identical or different radicals, R being chosen from monovalent hydrocarbonaceous groups, preferably from linear, branched and/or cyclic alkyls and/or aryls, and more preferably still from linear or branched C_1 - C_4 alkyls and phenyl, xylyl and tolyl groups;
- E corresponds to one or more monovalent functional substituents, which are identical to or different from one another, carrying one or more peroxo(-O-O-)

functional groups Fpo and each optionally comprising one or more Fpo-stabilizing functional groups Fstab which are identical to or different from one another and are chosen from functional groups capable of bonding via weak bonds with Fpo functional groups;

- G corresponds to one or more functional substituents, identical to or different from one another, each comprising one or more Fpo-stabilizing functional groups Fstab which are identical to or different from one another and are chosen from functional groups capable of bonding via weak bonds with the Fpo functional groups;

→ with the conditions according to which:

.(i). the concentration of [Fpo] functional groups, expressed by the ratio

$$\frac{\text{Fpo number}}{\text{Total number of silicon atoms in the POS}}$$

is defined as follows:

Δ $0 < [\text{Fpo}]$
 Δ preferably $0.01 \leq [\text{Fpo}] \leq 1.0$
 Δ and more preferably still $0.1 \leq [\text{Fpo}] \leq 0.6$,

.(ii). the concentration as mol% of T

siloxane units ($a + b + c = 1$) and/or Q

siloxane units ($a + b + c = 0$) is defined as follows:

- Δ $0 \leq [T \text{ and/or } Q] \leq 20$
 Δ preferably $0 \leq [T \text{ and/or } Q] \leq 10$
 5 Δ and more preferably still $0 \leq [T \text{ and/or } Q] \leq 8$.

These novel peroxide-comprising POSSs make it possible to stabilize the peroxo functional group and to control its oxidizing activity by restraining its activity for the production of free radicals. In
 10 addition, their bleaching and selectivity properties with respect to teeth make them particularly appropriate and effective bleaching systems for oral dental compositions, such as dentifrices.

This is because these silicones,
 15 functionalized by peroxo Fpos, have a specific affinity with respect to constituent materials of the teeth (in particular hydroxyapatite), so that they are selected vectors capable of conveying the chemical bleaching functional groups onto the teeth. It is obvious that
 20 this optimizes the effectiveness of said functional groups. It follows that it is possible to reduce the doses, which is entirely favorable to decreasing the aggressiveness of the bleaching agent.

Furthermore, these peroxide functionalized
 25 silicones are hydrophobic and thus have the advantage of protecting the Fpo functional groups from water,

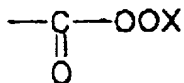
which is a major component in the instability of the Fpo functional groups.

The novel peroxide-comprising polyorganosiloxanes comprising Fpo functional groups
 5 can be linear and/or branched and/or crosslinked polymers according to the percentage by weight of DTQ siloxyl units which they comprise. Preferably, the peroxide-comprising POSSs according to the invention predominantly comprise D units ($a + b + c = 2$) and more
 10 preferably still are linear.

Advantageously, the E substituents of the siloxane units (I) are identical to or different from one another are chosen from (cyclo)aliphatic and/or aromatic and/or heterocyclic hydrocarbonaceous groups
 15 optionally comprising one or more heteroatoms, preferably O, N, S or Si, it being possible for these groups optionally to be substituted.

In just as advantageous a way, Fpo is included:

20 > either in an acyl peroxide:



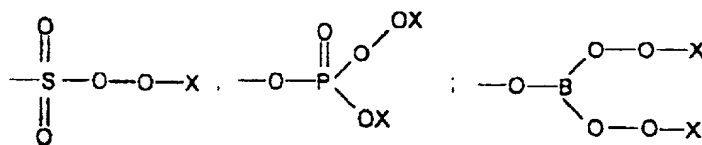
with X corresponding to H, to R^x , representing an aliphatic and/or alicyclic and/or aromatic and/or heterocyclic monovalent
 25 hydrocarbonaceous radical, that is to say comprising, inter alia, hydrogen and carbon

atoms, optionally comprising one or more heteroatoms (N, O, S and the like), it being possible for this radical optionally to be substituted and it being possible for R^x optionally to correspond to the same definition as that given above for R in the formula (I), to a halogen, preferably chlorine, or to a cation which makes it possible to form a salt with the peroxo anion and which is preferably chosen from the elements from columns Ia and IIA of the Periodic Table,

➤ or in a peroxide residue comprising sulfur, phosphorus, silicon or boron as oxygen carrier.

In other words, each peroxo functional group Fpo belongs to a peroxycarboxylic residue (acids, esters, halides, chlorides or salts) or alternatively a peroxide residue deriving from compounds comprising sulfur, phosphorus, boron or silicon.

It can be, e.g.:



with X as above.

Mention may be made, as examples of X groups which are cations, of: Na^+ , K^+ , Ca^{++} , Mg^{++} , and the like.

5 These peroxy-carboxylic and noncarboxylic
residues are connected to the silicon of the POS chain
via an aliphatic and/or alicyclic and/or aromatic
and/or heterocyclic hydrocarbonaceous linking unit
(that is to say, comprising in particular carbon and
10 hydrogen atoms) optionally comprising one or more
heteroatoms: N, O, S, and the like, optionally.

The assemblage comprising:

- 15 • first, the peroxy-carboxylic residue and/or
 the noncarboxylic peroxy,
 • and, secondly, the linking unit,
 form the functional substituent E.

In practice, the linking unit is, for example, of the -alkyl-O-aryl (benzyl), -alkyl anhydride or -alkylimide-aryl (benzyl) type, inter alia.

20 The advantageous stabilizing action of the Fstabs on the Fpos is a preferred characteristic of the functionalized POSs according to the invention. In accordance with the latter, the Fstabs are located on the (pendant) functional substituents E and/or G.

25 Without this being limiting, it is preferable for the Fstabs to be carried at least by the E group or groups.

so as to be close to the Fpos to be stabilized. It is not excluded to consider that the stabilizing effect of the Fstab is thus improved.

According to a preferred characteristic of the invention, the optional stabilizing functional groups Fstab of the E and/or G substituents of the formula (I) correspond to functional groups which can generate weak bonds (hydrogen bonds, e.g.) with Fpo and which are selected from the group consisting of:

- 10 → functional units comprising nitrogen and/or oxygen and/or fluorine and/or sulfur and/or phosphorus; carboxylic, carboxylate, amide, imide, sulfonamide, hydroxyl, alkoxy, amine or
- 15 organofluorinated units being preferred;
- cationic units, preferably those comprising one or more quaternary ammoniums;
- chelating units comprising one or more
- 20 ether functional groups and/or one or more amine functional groups, and/or phosphonate and/or sulfonate chelating units.

The optional functional substituents G each
25 comprise, in addition to the Fstab group or groups, a

The linking units of the G substituents are identical to or different from one another, which correspond to the same definition as that given above for the linking units of the E substituents.

- either from chlorosilanes or from alkoxy silanes carrying the E substituents, from chlorosilanes or from alkoxy silanes carrying G substituents and from chlorosilanes or from alkoxy silanes carrying the R substituents and/or hydrogen, by cohydrolysis, polycondensation and polymerization of the hydrolyzed products in the presence of cyclic diorganosiloxanes or redistribution in the presence of polydiorganosiloxanes, and the like,

or from functionalized polydiorganosiloxanes by hydrosilylation of hydrogenated polydiorganosiloxanes using complete or partial olefinic precursors of the functional substituents E and G.

Within the meaning of the present account, the terms "complete or partial olefinic precursors" correspond respectively:

- 5 • to the case where the olefinic precursor is in the final form and does not have to be subjected to other grafting operations to result in the complete substituent which will be converted to E or G after peroxidation (complete linking unit),
- 10 • and to the case where the linking unit of the E or G substituents is formed by several members placed end to end and corresponding to intermediate synthetic forms, the olefinic precursor constituting
- 15 the first member, which is bonded, first, to the silicone chain and, secondly, to the following member of the linking unit.

Without this being limiting, preference is given, in accordance with the invention, to peroxide-
20 comprising POSSs obtained by hydrosilylation of olefinic precursors of E and G substituents.

These hydrosilylation reactions can be carried out at a temperature of the order of 15 to 200°C, preferably of the order of 20 to 100°C, in the presence of a catalyst
25 based on a metal from the platinum group. Mention may in particular be made of the complex platinum

derivatives disclosed in US patents No. 3 715 334,
3 775 452, 3 814 730, 3 159 601 and 3 159 662.

The amounts of platinum catalysts employed are of the
order of 1 to 300 parts per million, expressed as
5 metal, with respect to the reaction medium.

The olefinic precursors employed in these
hydrosilylations advantageously do not comprise the Fpo
peroxo functional groups but their non-peroxygenated
forms F'po or any intermediate form of the latter. It
10 is preferable, in accordance with the invention, to
provide for protection of the F'po precursor functional
groups before the hydrosilylation.

The POSSs, grafted by hydrosilylation and carrying F'po
precursor functional groups, are optionally purified
15 and then subjected to oxidation, which makes possible
the conversion of the F'po functional groups to Fpo
functional groups.

According to a preferred embodiment of the
invention, the peroxide-comprising POSSs correspond to
20 the formula (II) given below:



in which:

- R^1 and R^3 independently representing a
25 hydrogen, a hydroxyl or a monovalent

residue corresponding to the same
definition as that given for R above;

- R^2 independently represent hydrogen, a
hydroxyl or a monovalent residue
corresponding to the same definition as
that given for R above;

- $2 \leq m + n + o \leq 300$
- preferably $3 \leq m + n + o \leq 50$
- and more preferably still $5 \leq m + n + o \leq 20$

- $0 \leq m \leq 200$
- preferably $1 \leq m \leq 100$
- and more preferably still $1 \leq m \leq 10$

- $0 \leq n \leq 50$
- preferably $1 \leq n \leq 10$
- and more preferably still $2 \leq n \leq 4$

- $0 \leq o \leq 50$
- preferably $1 \leq o \leq 10$
- and more preferably still $2 \leq o \leq 4$.

More preferably still, the polyorganosiloxanes are
characterized in that:

ΔR^1 and $R^3 = C_1-C_3$ alkyl, preferably $-CH_3$

$\Delta R^2 = C_1-C_3$ alkyl, preferably $-CH_3$

Δ the functional substituent or substituents E simultaneously comprise Fpo and Fstab functional groups.

In practice, without this being limiting, the functional substituents E of the peroxide-comprising POSs each comprise a linking unit comprising at least one bicarboxylated and/or benzoxylated and/or imide unit.

The case where the linking unit or units of the functional substituent or substituents E comprise at least one bicarboxylic unit corresponds to a preferred form of the invention in which the Fpo functional group is obtained from an anhydride which is converted, on the one hand, to Fpo and, on the other hand, to Fstab carboxylic functional group for stabilization of the neighboring Fpo.

The peroxide-comprising POSs according to the invention are stable and exhibit a high bleaching power.

According to another of its aspects, the present invention relates to a process for the preparation of the POSs as defined above. This process is characterized in that it consists essentially in oxidizing the polysiloxane precursors of the targeted peroxide-comprising POSs. This oxidation is carried out

using at least one oxidizing agent preferably chosen from the group consisting of:

H_2O_2 , O_2 , O_3 and their mixtures.

These -POS precursors are distinguished from the targeted peroxide-comprising POSs in that they comprise one or more F'po functional groups which are Fpo precursors and are composed:

□ of carboxyl residues: $\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{O}-\text{X} \end{array}$

with X' corresponding to the same definition as that given for X above;

□ and/or of acid anhydride residues: $\begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ -\text{C}-\text{O}-\text{C}- \end{array}$:

□ and/or of aldehyde residues;

□ and/or of residues comprising sulfur, phosphorus, silicon or boron.

These ester or anhydride functional groups of the -POS precursors can be terminal functional groups or functional groups which are included within a ring.

As is indicated above, the polysiloxane precursors comprising F'po functional groups can be obtained by cohydrolysis of nonfunctionalized chlorosilanes and alkoxysilanes and of chlorosilanes or alkoxysilanes functionalized by E and G substituents.

The stage which follows the cohydrolysis can be a polycondensation and a polymerization of the hydrolysis products, in the presence of cyclic diorganosiloxanes,

or a stage of redistribution in the presence of polydiorganosiloxanes. These conventional syntheses of POS by cohydrolysis/polycondensation/polymerization or by cohydrolysis/redistribution are described in particular in W. Nell, "Chemistry and Technology of Silicones", published by Academic Press, 1968.

According to a preferred alternative, the starting materials used can be hydrogenated polyorganosiloxanes which can be functionalized by reacting them according to a hydrosilylation reaction (addition with olefinic precursors of the E and G substituents). Reference will be made above for further details with regard to this hydrosilylation.

According to a preferred characteristic of the invention, the -POS precursors which are subjected to oxidation to produce targeted peroxide-comprising POSSs are selected from POSSs carrying functional substituents E:

- * anhydride substituents
- * and/or carboxyl substituents, preferably benzoyl substituents,
- * and/or aldehyde substituents, preferably benzaldehyde substituents,
- * and/or sulfonyl substituents,
- * and/or phosphoryl substituents,
- * and/or siloxyl substituents,

* and/or boroxide substituents.

More preferably still, the -POS precursors
selected:

- 5 ⇒ carry anhydride E groups, the oxidation
being carried out using H_2O_2 in the
presence of a catalyst of strong base
type, preferably potassium hydroxide,
- 10 ⇒ and/or carry carboxylic E groups,
preferably benzoyl groups, the oxidation
being carried out using H_2O_2 in the
presence of a catalyst of strong acid
type.

In accordance with the invention, it turned
out to be particularly advantageous for the -POS
15 precursors to exhibit, before the oxidation stage which
makes possible the conversion of the F'po groups to Fpo
groups, a molar purity $\geq 90\%$, preferably $\geq 95\%$.

In practice, this purification stage is
carried out by any known appropriate method, such as,
20 for example, devolatilization or fractional
precipitation from an organic solvent, such as
methanol.

As regards more specifically the oxidation
stage, it is seen that the oxidizing agents can be
25 hydrogen peroxide, oxygen, ozone and their mixtures.

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In the case where the oxidizing agent is composed of hydrogen peroxide, the catalyst employed can be a strong base, for example an inorganic base, such as KOH or NaOH, or alternatively a strong acid, for example an inorganic acid, such as H_2SO_4 , or an organic acid, such as MeSO_3H . The solvents employed in these scenarios are, for example, ethyl acetate or MeSO_3H .

When the oxidizing agent is oxygen, the use can be envisaged of a catalyst comprising Co^{2+} .

In practice, this oxidation stage can take place at ambient temperature and at ambient pressure.

Another subject matter of the present invention is the POS precursors comprising a F'po precursor functional group as defined above. These novel POS precursors as such constitute intermediates of the process according to the invention.

Finally, the present invention relates to the use of the peroxide-comprising POSSs as defined above as:

- bleaching agent,
- and/or disinfecting agent,
- and/or cleaning agent,
- and/or polymerization initiating agent,
- and/or agent for epoxidation.

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- 20

and more preferably still of the order of 1 to 5% by weight;

- polishing abrasives in a proportion of 5 to 40% by weight,

25

possible for these abrasives to be in

particular silica, precipitated calcium carbonate, magnesium carbonate, calcium phosphates, titanium, zinc or tin oxides, talc, kaolin, abrasive particles comprising a core of calcic material, preferably made of calcium carbonate, and a shell of idrophobic product, preferably a fatty acid salt and more preferably still a Na stearate; .

- one or more fluorinated compounds corresponding to a concentration of the order of 0.005 to 2%, preferably 0.1 to 1%, by weight of fluorine in said composition, it being possible for these fluorinated compounds to be in particular salts of monofluorophosphoric acid, in particular those of sodium, potassium, lithium, calcium, aluminum and ammonium, or alkali metal fluorides, in particular sodium fluoride;

- optionally anionic, nonionic, amphoteric or zwitterionic surface-active agents, in the proportion of approximately 0.1 to 10%, preferably of approximately 1 to 5%, of the weight of said composition; mention may be made, by way of examples, of:

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* nonionic surface-active agents, such as optionally polyethoxylated fatty esters of sorbitan, ethoxylated fatty acids, polyethylene glycol esters or polyether fatty alcohols,

* amphoteric surface-active agents, such as betaines or sulfobetaines

- optionally water in a proportion of approximately 0.1 to 50%, preferably approximately 0.5 to 40%, of the weight of said composition
- optionally humectants, in the proportion of approximately 10 to 85%, preferably of 10 to 70%, of the weight of said composition, humectants such as glycerol, sorbitol, polyethylene glycols, lactitol, xylitol, and the like
- optionally thickening agents, such as some silica used for this purpose (Tixosil 43®, sold by Rhône-Poulenc, and the like), in a proportion of 5 to 15% by weight, and/or polymers, used alone or in combination, such as xanthan gum, guar gum, cellulose derivatives (carboxymethylcellulose, hydroxyethylcellulose, hydroxypropylcellulose, hydroxypropylmethylcellulose, and the like), crosslinked polyacrylates, such as the Carbopol® products distributed by Goodrich, alginates or carrageenans, or

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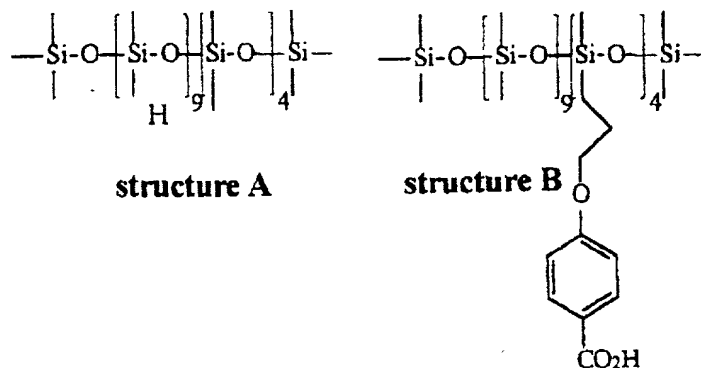
peroxide-comprising POSSs according to the invention as defined above as bleaching agents.

The present [lacuna] will be better understood with the help of the following nonlimiting
5 examples which also reveal some of the advantages and the alternative embodiments of the invention. The preparation of the precursor POSSs of the peroxide-comprising POSSs according to the invention, the conversion by oxidation of these precursors to
10 peroxide-comprising POSSs and the evaluation of the latter in terms of stability on storage and of bleaching power are presented in these examples.

EXAMPLES

- 15 **Example 1: Preparation of a -POS precursor (B) of a peroxide POS according to the invention, this precursor being a polydimethylsiloxane comprising trimethylsilyl ends carrying functional substituents of -propyl-oxy-benzoic type**

Starting silicone oil: Final silicone oil:



5 1.1. Synthesis of allyloxybenzoic acid

500 ml of distilled water, 5 l of absolute ethanol and, gradually, 450.9 g of potassium hydroxide (8.02 mol) are charged with vigorous stirring (240 rev/min) to a 10 l reactor, under an argon head space, equipped with a reflux condenser, a dropping funnel, a mechanical stirrer and thermometer probe. Once the potassium hydroxide has dissolved, 558.3 g of 4-hydroxybenzoic acid (4.04 mol) are charged. The reaction mass becomes cloudy and then becomes clear.

15 Allyl bromide (489.0 g, i.e. 4.04 mol) is then run in over 2 h at ambient temperature. After the allyl bromide has been run in, the reaction medium is brought to 80°C for 17 hours.

After returning to ambient temperature, the reaction medium is neutralized by gradual addition over 1 h 30 of 1 l of 36% hydrochloric acid (11 mol). The

reaction medium becomes milky and is filtered through a sintered glass No. 4 under vacuum. A white filtration cake is obtained and is washed with water (250 ml).

The allyloxybenzoic acid which is found in the filtration cake is purified by recrystallization. The filtration cake, 5 l of absolute ethanol and 750 ml of distilled water are charged to the 10 l reactor. The reaction mass is brought to reflux (80°C) and distilled water is gradually added until a single clear phase is obtained, i.e. 1.75 l of distilled water. The reaction mass is then decanted into a 10 l receptacle which is cooled with ice. The medium is allowed to recrystallize for 16 h and then filtration is carried out through a sintered glass No. 4 under vacuum. The cake is washed with distilled water (2 l, used over three occasions). Crystals are obtained and are dried under a 200 mmHg vacuum at 70°C. The yield is 35%.

20 1.2. Protection of allyloxybenzoic acid by a trimethylsilyl group

53.62 g of allyloxybenzoic acid, prepared in 1.1. (0.3 mol), are introduced into a 250 ml three-necked flask, under an argon head space, equipped with a reflux condenser, a mechanical stirrer and a thermometer probe, and 120.58 g of hexamethyldisilazane

bottomed flask equipped with a magnetic bar. The product is isolated by devolatilization at 120°C under a vacuum of 1 mmHg.

The product thus isolated is deprotected by hydrolysis with distilled water (200 ml), which is run onto the product to be deprotected over 1 h 15, and heating at 90°C for 16 hours. The medium becomes off white. The water is removed at 110°C under a vacuum of 2 mmHg over 4 h 15. 58.40 g of hydrosilylated oil of structure B are then obtained.

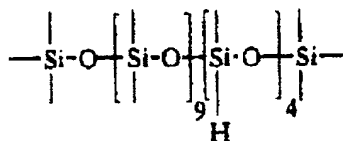
1.4. Purification of a silicone oil B comprising benzoic acid functional groups

The starting material is an oil which is 92% pure on a mass basis with 8% on a mass basis composed of ungrafted oligomers originating from ungrafted allyloxybenzoic acid or isomers of allyloxybenzoic acid. Several purification techniques are possible among the various purification techniques. The method employed here is fractional precipitation. It consists in dissolving the grafted oil obtained in 1.3. in a hot alcohol. This alcohol can be more particularly methanol. The polymer is then precipitated by addition of water of basic pH. The operation is repeated a further time. The third operation consists in dissolving the silicone polymer under hot conditions in

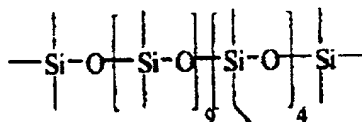
methanol and in then adding water at acidic pH. The polymer thus purified is heated at 115°C under a vacuum of 20 mmHg in order to remove the residual water or alcohol. The product is finally placed in an oven at 100°C at atmospheric pressure. A polymer with a purity of greater than 95% by weight is obtained.

Example 2: Preparation of a -POS precursor (C) of a peroxide POS according to the invention, this precursor being a polydimethylsiloxane comprising trimethylsilyl ends carrying functional substituents of -propyl-succinic anhydride type

Starting silicone oil: Final silicone oil:



structure A



structure C

15

Synthesis of the silicone oil C comprising succinic anhydride units

119.53 g of allylsuccinic anhydride, with a purity of more than 99 mol% (0.85 mol), and 44.2 mg of Karstedt platinum, comprising 10% by mass of platinum, are introduced into a 500 ml three-necked flask equipped with a mechanical stirrer, a reflux condenser,

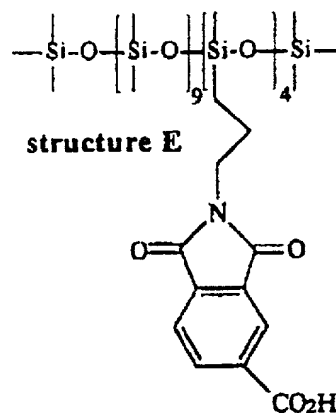
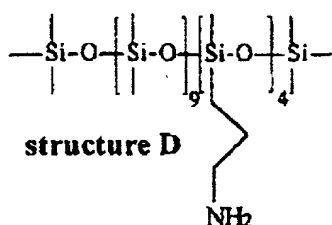
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Example 3: Preparation of a -POS precursor (E) of a peroxide POS according to the invention, this precursor being a polydimethylsiloxane comprising trimethylsilyl ends carrying functional substituents of -propyl-succinimide-benzoic type

Starting silicone oil: Final silicone oil:



10 3.1. Preparation of silicone comprising an amine functional group by coequilibration

50 g of aminopropyldimethoxymethylsilane (0.3 mol) are introduced into a three-necked flask, under an argon headspace, equipped with a devolatilization system, a mechanical stirrer, a dropping funnel and a temperature probe, and an amount of water of 27.6 g (1.5 mol) is added over 1 hour. The system is brought to 110°C and is devolatilized under 11 mmHg in order to collect the amount of methanol of 19.2 g.

After returning to [lacuna] temperature and having replaced the distillation system by a reflux condenser, 30.5 g of octamethyltetrasiloxane (0.1 mol, i.e. 10% excess), 34.3 g of a short silicone oil with 6
 5 silicons of formula M_2D_4 and 5.3 g of potassium silicate comprising 15% by weight of potassium hydroxide (80 ppm), in addition to 35.1 g of hydrolyzed silane obtained above, are introduced. After heating at 130°C for 6 hours while stripping with nitrogen, the
 10 reaction mixture is neutralized by addition of 12.3 g of a solution of silicated ester of phosphoric acid comprising 9% by mass of phosphoric acid. Following the neutralization, the medium is left in contact for 30 minutes at 80°C and then devolatilization is carried
 15 out under 2 mmHg at 170°C. 113.5 g of silicone oil with structure D are obtained.

3.2. Formation of a silicone E comprising acid and imide functional groups

20 28.8 g of trimellitic anhydride (0.15 mol) and 75 g of toluene are charged to a three-necked round-bottomed flask, under an argon head space, equipped with a reflux condenser, a mechanical stirrer, a dropping funnel, a thermometer probe and a Dien & Stark
 25 apparatus, and 50.0 g of silicone oil comprising an amine functional group with structure D (0.15 mol of

amine functional group) are run in over 1 hour. The reaction mixture is left in contact at ambient temperature for 1 hour and then the reaction mixture is brought to reflux for 5 hours; during the time, removal of the water is monitored. After returning to ambient temperature, the reaction mixture is filtered through a board filter under pressure. After having placed the reaction mixture in a single-necked round-bottomed flask equipped with a magnetic bar, the solvent is devolatilized by heating at 110°C under a vacuum of 10 mmHg. A polymer with structure E is obtained with a purity of 95% by weight.

Example 4: Preparation of a -POS precursor (F) of a peroxide-comprising POS according to the invention, this precursor being a polydimethylsiloxane comprising trimethylsilyl ends carrying functional substituents of aminoethylaminopropyl ($\text{H}_2\text{N}-(\text{CH}_2)_2-\text{NH}-(\text{CH}_2)_3-$) type

Example 3 is repeated apart from the difference that the aminopropyldimethoxymethylsilane employed in part 3.1. is replaced for aminoethylaminopropyldimethoxymethylsilane and, ultimately, a POS precursor or silicone oil F is obtained:

[lacuna]

Example 5: Preparation of a peroxide-comprising POS in which the Fpo (-O-O-) functional groups of the E substituents are included in percarboxylic acid

residues $\begin{array}{c} \text{O} \\ \parallel \\ (-\text{C}-\text{O}-\text{O}-\text{H}) \end{array}$ from the POS precursor

5 according to Example 2 (pendant anhydride residues)

5.1. Test

The following operations are carried out in a weighing tube:

- . 250 mg of silicone oil C of Example 2, i.e.
- 10 0.615 mmol of anhydride functional groups (4 functional groups per polymer), are weighed out,
- . 0.5 ml of ethyl acetate (AcOEt) is added,
- . 45 mg of 70% hydrogen peroxide, i.e. 0.926 mmol (1.5 equivalents excess with respect to the
- 15 stoichiometry, which is 1 H₂O₂ per anhydride), are weighed out,
- . 1 drop of KOH (1N) is introduced,
- . a small magnetic bar is added,
- . the mixture is stirred at ambient temperature for
- 20 1 hour.

5.2. Treatment

- . 3 ml of AcOEt are added
- . the mixture is transferred into a small 50 ml
- 25 separating funnel

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- . 3 ml of deionized water comprising 100 g/l of ammonium sulfate are added
- . the mixture is agitated and allowed to separate by settling, and the lower aqueous phase is removed
- 5 . the operation is restarted a further 2 occasions
- . the organic phase is recovered in a 50 ml beaker
- . 1 g of anhydrous MgSO_4 is added
- . the solution is transferred into a tared 50 ml round-bottomed flask and the separating funnel and MgSO_4
- 10 are rinsed twice with 1 ml of AcOEt
- . the solution is evaporated to dryness on a rotary evaporator, bath at a maximum of 35°
- . the residue is evaporated for a few minutes under pump vacuum under cold conditions (ambient temperature)
- 15 . the product obtained is weighed.

5.3. Quantitative determination of peroxides in the peroxide-comprising silicone oil

Apparatus: Metrohm Dosimat 665

20

5.3.1. Procedure

The following operations are carried out in a 50 ml Erlenmeyer flask:

- . approximately 250 mg of peroxide-comprising oil
- 25 are weighed out
- . the following are added:

- 20 ml of 80/20 acetic acid/H₂O mixture and dissolution is allowed to take place

- or, better still, 20 ml of pure acetic acid, dissolution is allowed to take place and then a small amount of water is added

. 1 spatula (1 g) of NaHCO₃ is added (inerting by CO₂)

. 1 spatula (1 g) of potassium iodide is added

. the flask is stoppered and placed in darkness for
10 a minimum of 20 minutes.

The contents of the Erlenmeyer flask are transferred into a 150 ml beaker (tall form):

. rinsing is carried out with 50 ml of distilled water

15 . acetone is added (maintenance of the solubility and antifoaming)

. a magnetic bar is added and the iodine released is quantitatively determined with a 0.1N sodium thiosulfate solution.

20

5.3.2. Calculations

Number of mmol of H₂O₂ = $V \text{ ml} \times CO_3 \times CO_2/COO \times CO_1$

Weight% of H₂O₂ = Number of millimoles quantitatively determined $\times 34/1000$

25 1 equivalent H₂O₂ = 1 equivalent R-CO-O-OH

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5.3.3. Expression of the results: Weight% as H₂O₂ equivalent

Given that the -POS precursor (oil C) prepared in Example 2 comprises the E substituents each carrying an anhydride and that the reaction is regarded as total (oxidation yield = 100%), then, for one mol of oil (C), 4 mol of H₂O₂ are reacted, i.e. as % by weight: 1 mol of oil (C) = 1628 g, for 4 mol of H₂O₂ = 136 g, i.e. 8.35 weight% of H₂O₂.

10

5.3.4. Result

The content of peracid in the oxidized oil C is 6.2%, i.e. an oxidation of $6.2/8.35 \times 100 = 74\%$.

15 **Example 6: Preparation of a peroxide-comprising POS in which the Fpo (-O-O-) functional groups of the E substituents are included in percarboxylic acid residues**

$$\begin{array}{c} \text{O} \\ || \\ (-\text{C}-\text{O}-\text{O}-\text{H}) \end{array}$$

from the POS precursor according to Example 2 (pendant anhydride residues)

20 The following are charged to a 100 ml round-bottomed flask:

- . 15 g of oil C of Example 2 (36.9 mmol of anhydride)
- . 30 g of ethyl acetate
- 25 . 2.7 g of 0 70% hydrogen peroxide (55.6 mmol ($\times 1.5$))

A magnetic bar is added and stirring is begun. There is an immediate exotherm and the temperature reaches 31°C.

The mixture is maintained for 1 hour.

The organic phase is washed 8 times with 20 ml of deionized water comprising 100 g/l of ammonium sulfate: the disappearance of the hydrogen peroxide in the aqueous phases is monitored by an indicator paper for peroxides.

The organic phase is filtered through a
20 sintered glass filter.

The organic phase is evaporated to dryness on a rotary
25 evaporator, bath at a maximum of 35°.

The residue is dried under pump vacuum for 3 hours at ambient temperature.

Weight obtained: 15.4 g

Content of peracids: 5.46% (expressed as H_2O_2)

5 Oxidation: 65%

Example 7: Study of the stability on storage of peroxide-comprising POSSs according to the invention

The POS used is prepared according to the methodology given in Example 6.

The product is stored dried at 5°C and 25°C.

Samples are withdrawn over time and the peroxides therein are quantitatively determined as described above in 5.3.

15

7.1. Storage at 5°C from 0 to 30 days

The results are given by Table 1 below.

Table 1

Duration (d)	% Peracids	% Oxidation
0	5.72	100.0
2	5.48	95.8
6	5.08	88.8
13	3.82	66.8
22	2.90	50.7
30	1.70	30.0

7.2. Storage at 5°C, 0, 11 and 22 days

The results are given by Table 2 below.

5 **Table 2**

Duration days	% Peracids 5°C	% Oxidation 5°C
0	5.46	100.0
11	4.24	74.1
22	2.85	49.8

Example 8: Preparation of a peroxide-comprising POS in which the Fpo (-O-O-) functional groups of the E substituents are included in percarboxylic acid

10 residues $\begin{array}{c} \text{O} \\ \parallel \\ (-\text{C}-\text{O}-\text{O}-\text{H}) \end{array}$ from the POS precursor according to **Example 2 (pendant anhydride residues)**

Example 5 is repeated apart from the difference that KOH is not used.

Results:

15 . Content as H₂O₂ equivalent = 0.59%

. Oxidation: 7%

Example 9: Preparation of a peroxide-comprising POS in which the Fpo (-O-O-) functional groups of the E substituents are included in percarboxylic acid

20

residues $\begin{array}{c} \text{O} \\ \parallel \\ (-\text{C}-\text{O}-\text{O}-\text{H}) \end{array}$ from the POS precursor according to
Example 2 (pendant anhydride residues)

Example 6 is repeated apart from the difference that the drop of KOH is replaced by a drop
 5 of H_3PO_4 (85% in water).

Results:

- . Content as H_2O_2 equivalent = 1.03%
- . Oxidation: 12%

10 **Example 10: Preparation of a peroxide-comprising POS in which the Fpo (-O-O-) functional groups of the E substituents are included in percarboxylic acid**

residues $\begin{array}{c} \text{O} \\ \parallel \\ (-\text{C}-\text{O}-\text{O}-\text{H}) \end{array}$ from the POS precursor according to
Example 1 (pendant benzoic residues)

15 **10.1. Test**

The following operations are carried out in a weighing tube:

- . 250 mg of silicone oil B of Example 1, i.e. 0.578 mmol of acid functional groups (4 functional
 20 groups per polymer), are weighed out
- . 0.5 ml of ethyl acetate (AcOEt) is added
- . 84 mg of 70% hydrogen peroxide, i.e. 1.729 mmol (3 equivalents excess with respect to the stoichiometry, which is 1 H_2O_2 per acid), are weighed out
- 25 . 1 drop of H_2SO_4 (95% in water) [lacuna]
- . a small magnetic bar is added

. the mixture is stirred at ambient temperature for 2 hours in the presence of an excess of anhydrous MgSO_4 ($> 100 \text{ mg}$).

5 10.2. Treatment

- . 3 ml of AcOEt are added
- . the mixture is transferred into a small 50 ml separating funnel
- . 3 ml of deionized water comprising 100 g/l of ammonium sulfate are added
- . the mixture is agitated and allowed to separate by settling, and the lower aqueous phase is removed
- . the operation is restarted a further 2 occasions
- . the organic phase is recovered in a 50 ml beaker
- 15 . 1 g of anhydrous MgSO_4 is added
- . the solution is transferred into a tared 50 ml round-bottomed flask and the separating funnel and MgSO_4 are rinsed twice with 1 ml of AcOEt
- . the solution is evaporated to dryness on a rotary
- 20 evaporator, bath at a maximum of 35°
- . the residue is evaporated for a few minutes under pump vacuum under cold conditions (ambient temperature)
- . the product obtained is weighed.

25 10.3. Result

- . Content of peracid: 0.66%

•

5 11.1. Method in development for determining the
bleaching power with respect to hydroxyapatite HAP
powder

11.1.1. Principle

- * Measurement of the bleaching power of oxidizing compounds with respect to a hydroxyapatite HAP powder contaminated beforehand by a hot tea solution.
- * Bleaching power quantified by colorimetric measurements carried out on a Minolta CR-241 device.

11.1.2. Equipment

A - Small items

- * Filter paper, "rapid filtration" No. 41 from Whatman, for the filtration of the tea solution and for the recovery of the contaminated powder
- * Filter paper, GF/C, diameter of 47 mm, from Whatman, used for the recovery of the bleached powder
- * Büchner funnel (diameter of 100 or 160 mm), 2 l vacuum filter flask, vacuum pump or filter pump with a differential manometer, and rubber seals
- * Pots made of crystal polystyrene (transparent), capacity of approximately 40 ml

B - Devices

- * Minolta CR-241 colorimeter
- * Promax 2020 to-and-fro stirrer
- 5 * Oven (50 to 100°C)

C - Products

- * Deionized water
- * Lipton Yellow Tea, Grade No. 1
- 10 * Bio-Rad hydroxyapatite HAP powder
- * Solution or oxidizing agent

11.1.3. Procedure

A - Contamination of the HAP powder

- 15 a - Measurement of the initial whiteness of
the powder

A measurement of the initial whiteness of the HAP powder is carried out. It is carried out on a Minolta CR-241 device. Three measurements are made in
20 order to obtain a mean value of L_0 , a_0 , b_0 .

b - Brewing of the tea and filtration

500 ml of deionized water and 10 cut tea bags are introduced into a 1 000 ml beaker ($C = \sim 40$ g/l) and brought to $\sim 80^\circ\text{C}$ with mechanical stirring
25 (200 rev/min) for 90 minutes.

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The stirring and the heating are halted. Once the medium has cooled to approximately 40°C (time necessary = ~ 90 min), it is filtered under vacuum.

The filtrate (= contaminating tea solution) is recovered. Its volume is readjusted to 500 ml with deionized water.

c - The contamination

7.5 g of HAP powder are introduced into the tea solution.

The combined mixture is again brought to ~ 80°C with stirring for 45 minutes.

The heating and the stirring are halted and the medium is cooled by the surrounding air (to ~ 40°C) before being filtered under vacuum.

The powder is washed with three times 20 ml of hot deionized water until the filtrate is colorless.

The filter and the powder are placed in the oven [T = 50-100°C] until the water has completely evaporated.

The powder, recovered in the form of agglomerates, is ground using a pestle and mortar.

Its new whiteness is measured (Ls, as, bs) with a Minolta CR-241.

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B - Bleaching of the contaminated HAP powder

6.5 g of oxidizing solution (comprising the equivalent of 0.3% of H_2O_2) and 50 mg of contaminated HAP powder are decanted into a flask made of crystal polystyrene with a capacity of approximately 40 ml.

The combined mixture is placed on the Promax 2020 to-and-fro stirrer for the desired time (15 min, 30 min, 1 h, 2 h, and the like) at the rate of 250 to-and-fro movements.

The medium is subsequently diluted by addition of 20 ml of ethanol before being filtered.

The powder is washed with three times 30 ml of ethanol.

The combined filter + bleached powder is dried in the open air under a hood.

The new whiteness of the bleached powder can be measured (Lc) and the bleaching power of the oxidizing solution can be calculated.

11.1.4. Calculations

The calculation of the bleaching power of the oxidizing compound is made from the value L given by the colorimeter obtained after the various treatments of the HAP powder.

L* represents the lightness of the sample, its values ranging between 0 and 100.

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The various values are thus defined:

- * Lo, initial lightness before contamination
- * Ls, lightness after contamination
- * Lc, lightness after bleaching.

5 The bleaching power is calculated as follows:

Bleaching power:

$$Pb = \frac{Lc - Ls}{Lo - Ls} \times 100$$

11.2. Measurement of the whiteness Lc obtained in the
 10 test described in 11.1. above with the peroxide-
comprising POS of Example 6

11.2.1. The bleaching of the HAP powder according to
 part 11.1.3.B above is carried out as follows:

6.5 g of oxidizing preparation comprising 300 mg of
 15 peroxide-comprising POS according to Example 6
 dispersed in 6.2 g of water inverted by manual
 agitation

and 50 mg of contaminated HAP powder are decanted into
 a flask made of crystal polystyrene with a capacity of
 20 40 mg.

The procedure is subsequently as indicated in
 part 11.1.3.B.

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11.2.2. Results

Table 3

Time (min)	Lc with water control	Pb*	Lc with peroxide- comprising POS	Pb*
0	50	0	50	0
15	49	0	69	45
60	49	0	69	45
120	49	0	70	48

$$* Pb = \frac{Lc - Ls}{Lo - Ls} \times 100$$

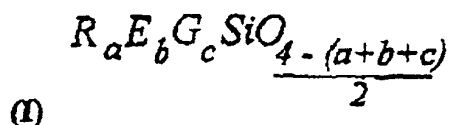
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Ls = 50 and Lo = 92

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CLAIMS

1. Polyorganosiloxanes (POSSs) comprising siloxane units of following formula (I):



→ in which

□ $a + b + c = 0$ to 3

□ $a, b, c = 0$ to 3

□ R corresponds to one or more identical or different radicals, R being chosen from monovalent hydrocarbonaceous groups, preferably from linear, branched and/or cyclic alkyls and/or aryls, and more preferably still from linear or branched C_1 - C_4 alkyls and phenyl, xylyl and tolyl groups;

□ E corresponds to one or more monovalent functional substituents, which are identical to or different from one another, carrying one or more peroxo(-O-O-) functional groups Fpo and each optionally comprising one or more Fpo-stabilizing functional groups Fstab which are identical

5

10

— 11 —

15

is defined as follows:

Δ preferably $0.01 \leq [\text{Fpo}] \leq 1.0$

(ii). the concentration as mol% of T

Δ $0 \leq [T \text{ and/or } Q] \leq 20$

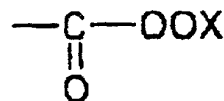
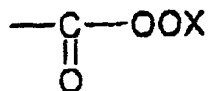
Δ and more preferably still $0 \leq [T \text{ and/or } Q] \leq 8$.

2. Polyorganosiloxanes according to claim 1, characterized

■ in that the E substituents of the units (I) are identical to or different from one another are chosen from (cyclo)aliphatic and/or aromatic and/or heterocyclic hydrocarbonaceous groups optionally comprising one or more heteroatoms, preferably O, N, S or Si, it being possible for these groups optionally to be substituted;

10 ■ and in that Fpo is included:

➤ either in an acyl peroxide



➤ either in an acyl peroxide:

with X corresponding to H, [lacuna]

15 representing an aliphatic and/or alicyclic and/or aromatic and/or heterocyclic monovalent hydrocarbonaceous radical, that is to say comprising, inter alia, hydrogen and carbon atoms, optionally comprising one or more heteroatoms (N, O, S, and the like), it being possible for this radical optionally to be substituted;

20 it being possible for R^x optionally to correspond to the same definition as that given above for R in the formula (I), to a

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halogen, preferably chlorine, or to a cation which makes it possible to form a salt with the peroxo anion and which is preferably chosen from the elements from columns Ia and IIA of the Periodic Table,

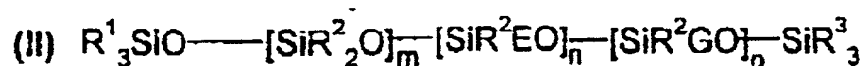
➤ or in a peroxide residue comprising sulfur, phosphorus, silicon or boron as oxygen carrier.

3. Polyorganosiloxanes according to claim 1 or claim 2, characterized in that, in the G substituent or substituents of the formula (I), the Fstabs correspond to functional groups which can generate weak bonds (hydrogen bonds) with Fpo and which are selected from the group consisting of:

- functional units comprising nitrogen and/or oxygen and/or fluorine and/or sulfur and/or phosphorus; carboxylic, carboxylate, amide, imide, sulfonamide, hydroxyl, alkoxy, amine or organofluorinated units being preferred;
- cationic units, preferably those comprising one or more quaternary ammoniums;
- chelating units comprising one or more ether functional groups and/or one or more amine functional groups, and/or

phosphonate and/or sulfonate chelating units.

4. Polyorganosiloxanes according to any one of claims 1 to 3, characterized in that they correspond to the formula (II) given below:



in which:

- 10 • R^1 and R^3 independently representing a hydrogen, a hydroxyl or a monovalent residue corresponding to the same definition as that given for R above;
- R^2 independently represent hydrogen, a hydroxyl or a monovalent residue corresponding to the same definition as that given for R above;
- 15 • $2 \leq m + n + o \leq 300$
- preferably $3 \leq m + n + o \leq 50$
- 20 • and more preferably still $5 \leq m + n + o \leq 20$
- $0 \leq m \leq 200$
- preferably $1 \leq m \leq 100$
- and more preferably still $1 \leq m \leq 10$
- 25 • $0 \leq n \leq 50$

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- preferably $1 \leq n \leq 10$
- and more preferably still $2 \leq n \leq 4$

- $0 \leq o \leq 50$
- preferably $1 \leq o \leq 10$
- and more preferably still $2 \leq o \leq 4$.

5

5. Polyorganosiloxanes according to claim 4,

characterized in that:

10

Δ R^1 and $R^3 = C_1-C_3$ alkyl, preferably $-CH_3$

Δ $R^2 = C_1-C_3$ alkyl, preferably $-CH_3$

Δ the functional substituent or substituents E simultaneously comprise Fpo and Fstab functional groups.

6. Polyorganosiloxanes according to any one of claims 1 to 5, characterized in that E comprises, in addition to the Fpo group or groups, at least one bicarboxylated and/or benzoxyl and/or imide unit.

7. Process for the preparation of the POSSs according to any one of claims 1 to 6, characterized in that it consists essentially in oxidizing polysiloxane precursors of the POSSs according to any one of claims 1 to 6, using at least one oxidizing agent preferably chosen from the group consisting of:

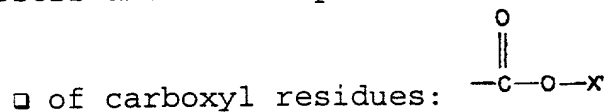
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H_2O_2 , O_2 , O_3 and their mixtures,

these -POS precursors being distinguished from the targeted peroxide-comprising POSSs in that they

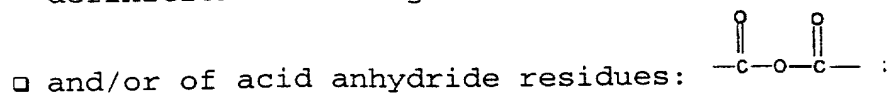
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comprise one or more F'po functional groups which are Fpo precursors and are composed:



with X' corresponding to the same

5 definition as that given for X in claim 2;



□ and/or of aldehyde residues;

and/or of oxide residues comprising sulfur, phosphorus, silicon or boron.

10 8. Process according to claim 7,

characterized in that the -POS precursors which are subjected to oxidation to produce targeted peroxide-comprising POSSs are selected from POSSs carrying functional substituents E:

- 15
- * anhydride substituents
 - * and/or carboxyl substituents, preferably benzoyl substituents,
 - * and/or aldehyde substituents, preferably benzaldehyde substituents,
- 20
- * and/or sulfonyl substituents,
 - * and/or phosphoryl substituents,
 - * and/or siloxyl substituents,
 - * and/or boroxide substituents.

9. Process according to claim 8,

25 characterized in that the -POS precursors selected:

⇒ carry anhydride E groups, the oxidation being carried out using H_2O_2 in the presence of a catalyst of strong base type, preferably potassium hydroxide,

5 ⇒ and/or carry carboxylic E groups, preferably benzoyl groups, the oxidation being carried out using H_2O_2 in the presence of a catalyst of strong acid type.

10 10. Process according to any one of claims 1 to 9, characterized in that use is made of -POS precursors with a molar purity $\geq 90\%$, preferably $\geq 95\%$.

11. POS precursors as defined in any one of claims 7 to 10.

15 12. Use of the peroxide-comprising POSs according to any one of claims 1 to 6 and/or obtained by the process according to any one of claims 7 to 10 as:

- 20
- bleaching agent,
 - and/or disinfecting agent,
 - and/or cleaning agent,
 - and/or polymerization initiating agent,
 - and/or agent for epoxidation.

25 13. Dental composition, in particular a dentifrice, characterized in that it comprises peroxygenated POSs according to any one of claims 1 to

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6 and/or [lacuna] by the process according to any one of claims 7 to 10 as bleaching agent.

14. Detergent composition, characterized in that it comprises peroxygenated POSs according to any one of claims 1 to 6 and/or [lacuna] by the process according to any one of claims 7 to 10 as bleaching agent.

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**PEROXIDE-COMPRISING POLYORGANOSILOXANES (POS), ONE OF THEIR
PROCESSES OF PREPARATION AND THEIR USES, IN PARTICULAR AS
BLEACHING AGENT IN DENTAL COMPOSITIONS**

Abstract of the Disclosure

The invention concerns polyorganosiloxanes (POS) grafted with peroxide functions and functions stabilizing the latter. Said stabilized peroxidised POS are designed to form a novel oxidizing system useful as bleaching agents, for example or dental or detergent compositions. The invention aims at and succeeds in providing peroxygenated bleaching agents more stable and more efficient than those known in prior art. The inventive stabilized and peroxidised POS correspond for example to the formula (a). The invention also concerns a method for making said peroxidised POS, the precursors thereof and their uses as bleaching agents in dental compositions (toothpaste or detergent compositions).

#3

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COMBINED DECLARATION FOR PATENT APPLICATION AND POWER OF ATTORNEY
(include Reference to PCT International Applications) PCT/FR99/02984

ATTORNEY'S DOCKET NO
RN98173

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

**PEROXIDE-COMPRISING POLYORGANOSILOXANES (POS), ONE OF THEIR
PROCESSES OF PREPARATION AND THEIR USES, IN PARTICULAR AS
BLEACHING AGENT IN DENTAL COMPOSITIONS**

the specification of which (check only one item below):

☐ is attached hereto.

☐ was filed as United States application

Serial No. _____

on _____

and was amended

on _____ (if applicable)

☒ was filed as PCT international application

Number PCT/ FR99/02984

on December 1, 1999

and amended under PCT ARTICLE 19

on _____ (if applicable).

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to the patentability of this application in accordance with Title 37, Code of Federal Regulations. §1.56(a).

I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate or of any PCT international application(s) designating at least one country other than the United States of America listed below and have also identified below any foreign application(s) for patent or inventor's certificate or any PCT international application(s) designating at least one country other than the United States of America filed by me on the same subject matter having a filing date before that of the application(s) of which priority is claimed:

PRIOR FOREIGN/PCT APPLICATION(S) AND ANY PRIORITY CLAIMS UNDER 35 U.S.C. 119:

COUNTRY PCT indicate PCT	APPLICATION NUMBER	DATE OF FILING (day month year)	PRIORITY CLAIMED UNDER 35 USC 119-	
FRANCE	98/15,715	9 December , 1998	<input checked="" type="checkbox"/> YES	<input type="checkbox"/> NO
			<input type="checkbox"/> YES	<input type="checkbox"/> NO
			<input type="checkbox"/> YES	<input type="checkbox"/> NO
			<input type="checkbox"/> YES	<input type="checkbox"/> NO
			<input type="checkbox"/> YES	<input type="checkbox"/> NO

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<p>PRIOR U.S. APPLICATIONS OR PCT INTERNATIONAL APPLICATIONS DESIGNATING THE U.S. FOR BENEFIT UNDER 35 U.S.C. 120</p>					
U.S. APPLICATIONS			STATUS (CHECK ONE)		
U.S. APPLICATION NUMBER	U.S. FILING DATE	PATENTED	PENDING	ABANDONED	
PCT APPLICATIONS DESIGNATING THE U.S.					
PCT APPLICATION NO	PCT FILING DATE	US SERIAL NUMBERS ASSIGNED (if any)			
<p>POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney's and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith (List name and registration number) JOHN A. SHEDDEN - Reg. No. 25,644, Kevin McVEIGH - Reg. No. 33017 JOHN D. WOOD - Reg. No. 31,146</p>					
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SIGNATURE OF INVENTOR 201		SIGNATURE OF INVENTOR 202		SIGNATURE OF INVENTOR 203	
<i>[Signature]</i>		<i>[Signature]</i>		<i>[Signature]</i>	
DATE		DATE		DATE	
<i>July 6th 2001</i>		<i>June 19-2001</i>		<i>June 20-2001</i>	

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PRIOR U.S. APPLICATIONS OR PCT INTERNATIONAL APPLICATIONS DESIGNATING THE U.S. FOR BENEFIT UNDER 35 U.S.C. 120					
U.S. APPLICATIONS			STATUS (CHECK ONE)		
U.S. APPLICATION NUMBER	U.S. FILING DATE	PATENTED	PENDING	ABANDONED	
PCT APPLICATIONS DESIGNATING THE U.S.					
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Send Correspondence to: JOHN A. SHEDDEN INTELLECTUAL PROPERTY DEPT. RHODIA INC. 259 PROSPECT PLAINS ROAD, CN 7500, CRANBURY, NJ 08512-7500				Direct Telephone Calls to: <small>(name and telephone number)</small> JOHN A. SHEDDEN (609) 860-4190	
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	DALLEMER	Frédéric			
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	RESIDENCE & CITIZENSHIP	CITY	STATE OR FOREIGN COUNTRY	COUNTRY OF CITIZENSHIP	
	POST OFFICE ADDRESS	POST OFFICE ADDRESS	CITY	STATE & ZIP CODE/COUNTRY	
206	FULL NAME OF INVENTOR	FAMILY NAME	FIRST GIVEN NAME	SECOND GIVEN NAME	
	RESIDENCE & CITIZENSHIP	CITY	STATE OR FOREIGN COUNTRY	COUNTRY OF CITIZENSHIP	
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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.					
SIGNATURE OF INVENTOR 204		SIGNATURE OF INVENTOR 205		SIGNATURE OF INVENTOR 206	
DATE 19th of June, 2001		DATE		DATE	

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